Effect of Thermal History on Properties of *block*-Copolyetheresters with Poly(tetramethylene 2,6-naphthalenedicarboxylate) Segments

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ABSTRACT: The effect of compression molding on the thermal transitions and crystalline properties of *block*-copolyetheresters with hard segments of poly(tetramethylene 2,6-naphthalenedicarboxylate) and soft segments of poly(tetramethylene oxide) were investigated by differential scanning calorimetry (DSC), X-ray diffraction, thermal stimulated current (TSC), and dynamic mechanical analysis (DMA). The X-ray diffraction patterns of compression molded samples of the *block*-copolymers were considerably different from those of the corresponding samples with slow-cooling history. After compression molding, the diffraction peaks were changed completely indicating a different crystalline structure for the polyester segments, and the diffraction peaks became sharper indicating a higher crystallinity. The DSC results also showed that the melting point and crystallinity of the polyester segments were increased after compression molding. The glass transition temperatures of the polyether soft phase and polyester hard phase also were determined by DSC, TSC, and DMA separately with consistent data and were found to be dependent on the content of polyether segments and the molecular weight of the poly(tetramethylene ether)glycol (PTMEG) used. A γ-transition was observed by TSC and DMA and seemed to be independent of the composition and the thermal history. The glass transition temperatures of the polyether soft phase and the polyester hard phase of the *block*-copolymers derived from PTMEG 650 and PTMEG 1000 shifted to a lower temperature after compression molding possibly because of the partial miscibility between the comprising segments in these two series. The abrupt drop in log G' in the temperature range of $-10-15$°C for the *block*-copolymers derived from PTMEG 2000 was caused by the melting of the polyether segments and indicated that the crystalline properties of the polyether segments could affect their mechanical properties. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1441–1449, 1999

Key words: *block*-copolyetheresters; thermal history; compression molding; miscibility

INTRODUCTION

The concept of the *block*-copolymer can be used to design thermoplastic elastomers.[1,2] A typical com-

mercial example is the *block*-copolyetheresters.[1–8] The majority of studies have been made on the *block*-copolyetheresters based on poly(tetramethylene terephthalate) or poly(tetramethylene isophthalate) hard segments.[1,2,8–16] However, the lower melting point of poly(tetramethylene terephthalate) or poly(tetramethylene isophthalate) limits the ultimate heat resistance for these *block*-copolyether-

Table I   Charge Composition, Polymer Composition Measured by ^{1}H-NMR and η_{inh} of *Block*-Copolyetheresters

Sample	M_n of PTMEG	Charge Composition[a]	Polymer Composition[a]	η_{inh} (dL/g)
N4	—	1.0 : 1.8 : 0.0	1.00 : 1.01 : 0.00	0.56
N4E1(0.1)	650	1.0 : 1.8 : 0.1	1.00 : 0.90 : 0.11	0.76
N4E1(0.2)	650	1.0 : 1.8 : 0.2	1.00 : 0.80 : 0.21	0.92
N4E1(0.3)	650	1.0 : 1.8 : 0.3	1.00 : 0.71 : 0.29	1.17
N4E2(0.1)	1000	1.0 : 1.8 : 0.1	1.00 : 0.89 : 0.12	1.01
N4E2(0.2)	1000	1.0 : 1.8 : 0.2	1.00 : 0.80 : 0.21	0.88
N4E2(0.3)	1000	1.0 : 1.8 : 0.3	1.00 : 0.72 : 0.30	1.04
N4E3(0.1)	2000	1.0 : 1.8 : 0.1	1.00 : 0.91 : 0.12	0.87
N4E3(0.2)	2000	1.0 : 1.8 : 0.2	1.00 : 0.81 : 0.21	1.04
N4E3(0.3)	2000	1.0 : 1.8 : 0.3	1.00 : 0.72 : 0.31	1.16

[a] Dimethyl 2,6-naphthalenedicarboxylate : BDO : PTMEG.

esters. There have been some reports about the synthesis and properties of *block*-copolyetheresters with hard segments of poly(alkylene 2,6-naphthalenedicarboxylate) and poly(alkylene 4,4′-bibenzoate), which show a higher melting point.[5,7,17,18] In addition to a higher melting point for higher heat resistance, crystallization behavior should be considered, which may influence the mechanical properties and moldability.[11,12,15,16] Poly(tetramethylene 2,6-naphthalenedicarboxylate) exhibits a rather high melting point of 246°C and can crystallize easily.[19] Thus, here we use poly(tetramethylene 2,6-naphthalenedicarboxylate) to design *block*-copolyetheresters. Wolfe[5,7] has described a series of *block*-copolyetheresters of 50% of hard segments with hard segments of poly(alkylene 2,6-naphthalenedicarboxylate) and soft segments of poly(tetramethylene oxide), but only a composition of poly(tetramethylene 2,6-naphthalenedicarboxylate) has been presented. However, little is known about the effects of the sequence length of poly(tetramethylene ether) and the polymer composition on their properties. In a previous article,[20] the synthesis and properties of a series of *block*-copolyetheresters with hard segments of poly(tetramethylene 2,6-naphthalenedicarboxylate) (N4) and soft segments of poly(tetramethylene oxide) (PTMO) of various sequence lengths were presented. These *block*-copolyetheresters have the general formula

where n is the degree of polymerization of the poly(tetramethylene ether) glycol (PTMEG) used

in the synthesis and x is the molar fraction of the PTMEG in the diol units.

A very interesting phenomenon was observed that the X-ray diffraction patterns of compression molded specimens of the *block*-copolymers were considerably different from those of the corresponding samples with a slow-cooling history. In this article, the effect of compression molding on the thermal transitions and crystalline properties of *block*-copolyetheresters were studied by differential scanning calorimetry (DSC), X-ray diffraction, thermal stimulated current (TSC), and dynamic mechanical analysis (DMA).

EXPERIMENTAL

The *block*-copolyetheresters were prepared by melt polycondensation of dimethyl 2,6-naphthalenedicarboxylate (DMN), 1,4-butanediol (BDO), and a PTMEG with a molecular weight of 650, 1000, or 2000 in the presence of 0.1% of tetrabutyl orthotitanate and 0.1% of lead acetate as the catalysts as described previously.[20] The *block*-copolymers are denoted as N4Em(x), where N4 means the poly(tetramethylene 2,6-naphthalenedicarboxylate) hard segment; E1, E2 and E3, which represent the molecular weight of PTMEG used, are 650, 1000, and 2000, respectively; and x is the charge molar ratio of the PTMEG to DMN. The charge composition, measured composition, and η_{inh} of the *block*-copolyetheresters are summarized in Table I.

The *block*-copolyetheresters were compression molded under a pressure of 20 Kgf/cm^2 (or will be specified in the text) at a temperature near the

Table II   Thermal Transitions of Slowly Cooled Samples and Compression Molded Samples[a] Determined by DSC

Sample	T_gS (°C)	T_mS (°C)	ΔH_mS (J/g)	T_gH (°C)	T_mH (°C)	ΔH_mH (J/g)
N4	—	—	—	—	244	32.1
N4C	—	—	—	70	246	47.4
N4E1(0.1)	−8	—	—	—	230	36.4
N4E1(0.1)C	−38	—	—	49	235	54.2
N4E1(0.2)	−32	—	—	57	209	19.9
N4E1(0.2)C	−38	—	—	50	216	40.6
N4E1(0.3)	−37	—	—	—	187	4.45
N4E1(0.3)C	−42	—	—	50	205	29.6
N4E2(0.1)	−46	—	—	—	229	26.5
N4E2(0.1)C	−50	—	—	55	230	47.1
N4E2(0.2)	−53	—	—	—	206	12.3
N4E2(0.2)C	−56	—	—	54	212	33.7
N4E2(0.3)	−57	—	—	62	186	10.5
N4E2(0.3)C	−58	—	—	54	197	24.7
N4E3(0.1)	−67	16	9.85	—	234	13.3
N4E3(0.1)C	−66	12	12.1	59	235	34.8
N4E3(0.2)	−67	13	17.6	—	220	8.12
N4E3(0.2)C	−65	13	17.4	57	225	24.0
N4E3(0.3)	−68	14	21.3	—	169	7.74
N4E3(0.3)C	−65	17	25.1	57	179	14.7

[a] Indicated by "C" after the original notation.

melting point of the polyester segments determined by DSC (see Table II, slowly cooled samples); the holding time was 10 min and the cooling rate was 20°C/min. The thermal properties of compression molded and slowly cooled samples were determined by a Du Pont 910 DSC at a heating rate of 20°C/min under nitrogen. The X-ray diffraction patterns of compression molded and slowly cooled samples were recorded on a Shimadzu XD-5 X-Ray diffractometer using Cu K_α radiation. The TSC curves from −120 to 120°C of compression molded and slowly cooled samples polarized at 250 V/mm and 100°C were determined by a Solomat TSC/RMA 91000 at a heating of 7°C/min. The dynamic mechanical properties of the compression molded samples were measured by a Rheometric RDS II at 1 Hz at a heating rate of 5°C/min.

RESULTS AND DISCUSSION

DSC

The effect of composition on the thermal transitions and X-ray diffraction patterns of slowly cooled samples (20°C/min cooling rate) was presented elsewhere.[20] Table II summarizes the thermal transitions including the glass transition temperature of polyether soft segments (T_gS), the melting temperature of the polyether soft segments (T_mS) and ΔH_mS, the glass transition temperature of polyester hard segments (T_gH), the melting temperature of the polyester hard segments (T_mH), and ΔH_mH of slowly cooled samples measured by DSC. The DSC heating curves of compression molded samples are shown in Figures 1 and 2. In the temperature range of −100–40°C, the DSC heating curves of compression molded N4E1(x) and N4E2(x) samples, denoted as N4E1(x)Cs and N4E2(x)Cs, exhibit a step inflection, and those of compression molded N4E3(x) samples, denoted as N4E3(x)Cs, exhibit a step inflection and an endotherm as shown in Figures 1 and 2. The midpoint of the step inflection is taken as the glass transition temperature of the polyether soft segment T_gS, and the peak temperature of the endotherm is taken at the melting temperature of the polyether soft segments T_mS. The values of T_gS, T_mS, and ΔH_mS are listed in Table II. In the temperature range of 50–260°C, the DSC heating curves of the compression molded *block*-copolyetheresters show a step inflection and endothermic peak(s) caused by

Figure 1 The DSC heating curves of N4Cs and N4E1(x)Cs.

the melting of the polyester hard segments. The midpoint of the step inflection is taken as the glass transition temperature of the polyester hard segments T_gH, and the peak temperature of the higher temperature peak is taken as T_mH. The T_gH, T_mH, and ΔH_m data also are tabulated in Table I. The trend of the effect of composition on the thermal transitions of the compression molded samples is similar to those of slowly cooled samples.

It could be seen that the melting transition was affected significantly by compression molding. The N4C, compression molded poly(tetramethylene 2,6-naphthalenedicarboxylate), exhibited a T_m of 246°C, which is slightly higher than that of slowly cooled N4, and a ΔH_m of 47.4 J/g, which is significantly greater than that of slowly cooled N4. Clearly, compression molding under our conditions increased the crystallinity of N4. For all *block*-copolyetheresters, the T_mH was raised to a higher temperature, and the ΔH_mH was increased significantly after compression molding. The increase in the crystallinity of the polyester hard segments was even more obvious for the *block*-copolyetheresters, especially those with higher x. As shown in Figures 1 and 2, the melting transition portion in DSC heating curves of

the compression molded samples of the *block*-copolyetheresters with higher x-values seems to be an overlapped profile of a lower-temperature broad endotherm and a higher-temperature sharper endotherm, rather than a broad endotherm for slowly cooled samples. The effect of compression molding on the crystalline properties of the polyester hard segments will be discussed later in combination with X-ray diffraction data.

The effect of compression molding on T_gS and T_gH is complex. The T_gH of most slowly cooled samples could not be determined by DSC; however, the T_gH of the compression molded samples can be seen concisely from their DSC heating curves. The reason for this phenomenon is not clear. The T_gS values of N4E3(x)Cs determined by DSC are almost the same as those of the corresponding slowly cooled sample and are around −68°C and independent of x. As described previously,[20] the amorphous parts of the polyether segments in this N4E3(x) series of *block*-copolyetheresters would be immiscible with the amorphous parts of the polyester segments; thus

Figure 2 The DSC heating curves of N4E2(x)Cs and N4E3(x)Cs.

compression molding did not affect the T_gS. However, compression seemed to depress the T_gS and T_gH for N4E1(x) and N4E2(x) series of *block*-copolyetheresters as shown in Table I. One possible reason is that the amorphous parts of the polyether segments in these two series might be miscible partially with the amorphous parts of the polyester segments.[20] Because compression molding increased the crystallinity of the polyester segments, the content of amorphous polyester parts decreased accordingly. This effect decreased the content of polyester segments in the amorphous polyether phase and lowered the T_gS.

X-Ray Diffraction

As described previously,[20] slowly cooled N4 sample showed two sharp diffraction peaks at 2θ = 15.3 and 24.1° and two smaller diffraction peaks at 2θ = 19.8 and 28.6° and the diffraction patterns of the slowly cooled *block*-copolyether-ester samples were similar to N4 especially in peak positions but the intensities were composition dependent. As x increased, the diffraction peak became broader or even disappeared indicating decreasing of the crystallinity as expected. The X-ray diffraction patterns of some compression molded samples N4C and N4E1(x)Cs are shown in Figure 3. Clearly, the X-ray diffraction patterns of the *block*-copolyetheresters were changed considerably after compression molding.

The N4C exhibited four additional small diffraction peaks at 2θ = 12.6, 16.7, 22.1, and 25.7° and the original peaks of the slowly cooled sample almost remained unchanged. Thus the crystallinity of N4 was increased after compression molding. This is consistent with the DSC result. The compression molded *block*-copolyetherester samples exhibited completely different X-ray diffraction patterns from the slow-cooled samples. Three sharp peaks at 2θ = 12.7, 16.8, and 25.8°, and a broader peak at 2θ = 23.1° were observed. The diffraction peaks were sharper for compression molded samples than the corresponding slowly cooled ones irrespective of their positions. Because the polyether segments are amorphous at room temperature, the diffraction peaks of the *block*-copolyetheresters are attributed to the polyester segments. Thus, compression molding increased the crystallinity of the polyester segments. As x increased, the amorphous scattering increased and some diffraction peaks became broader because of the decrease in the sequence length of the polyester segments which was more

Figure 3 X-ray diffraction patterns of N4Cs and N4E1(x)Cs.

obvious for N4E3(x)C series than for N4E2(x)C and N4E1(x)C series because of the higher content (in weight) of the polyether segment of the former.

The change in X-ray diffraction patterns after compression molding would be caused by the effect of pressure during compression molding. Figure 4 depicts the effect of compression molding pressure on the X-ray diffraction patterns of N4E2(0.1) samples. The X-ray diffraction pattern of the slowly cooled N4E2(0.1) sample is similar to that of slowly cooled N4 sample. A compression molding pressure of 1 Kgf/cm^2 (0.098 MPa) changed the diffraction patterns considerably as shown in Figure 4. After compression molding at various pressures, three major diffraction peaks at 2θ = 12.7, 16.8, and 25.8° and one broader peak at 2θ = 23.1° appeared. The original diffraction peaks at 2θ = 15.4, 20.0, 24.1, and 28.5° were depressed or even disappeared. For example, as the pressure increased, the diffraction peak at 2θ = 15.4° was weakened and disappeared at a compression pressure of 20 Kgf/cm^2 as shown in Figure 4. In other words, the pressure during com-

Figure 4 X-ray diffraction patterns of slowly cooled N4E2(0.1), compression molded N4E2(0.1) at various pressures, and remelted treated N4E2(0.1).

pression favored the formation of new diffraction peaks. This might be caused by the repacking of polyester segments in crystalline structure. Under the compression molding condition, the pressure forced the polyester segments to pack in a denser state and hence a denser crystalline structure, which resulted in different X-ray diffraction peaks. If the compression molded samples are remelted and sheared to relax the denser state and slowly cooled, this thermal history will be similar to the slowly cooled samples. In fact, the so remelted treated N4E2(0.1) sample exhibited a diffraction pattern similar to that of the slowly cooled N4E2(0.1) as shown in Figure 4. This confirms the effect of compression molding on the change of the diffraction patterns. In sample N4C, only a small portion of molecule chains was packed in the denser crystalline structure as shown in Figure 3. This might be caused by the kinetic effect. The N4 had a high molecular weight (η_{inh} = 0.56 dL/g), and it was difficult for most molecule chains to pack in the dense state

under pressure. In fact, a low molecular weight poly(tetramethylene 2,6-naphthalenedicarboxylate) with an η_{inh} of 0.13 dL/g after compression molding exhibited a diffraction pattern similar to those of the compression molded *block*-copolyetherester samples such as N4E2(0.1)C rather than those N4C. Because the sequence length of the polyester segments in the *block*-copolyetheresters is significantly shorter than N4 and flexible polyether segments were present the polyester segments could adopt well in a denser form. Thus a different crystalline structure resulted.

TSC

The TSC curves of slowly cooled and compression molded samples were measured. In a TSC measurement, the sample is polarized by an electric field at a given temperature above the T_g and the permanent dipoles are oriented. Then the sample is cooled under the electric field, which renders that the sample remained polarized, to a lower temperature. Then the sample is heated, and the depolarization current caused by the relaxation of the molecules is monitored. Any thermal transition associated with molecular motion can cause a depolarization current peak.[21] The TSC curves of N4E2(0.1)C, N4E2(0.3)C, and N4E3(0.2)C are shown in Figure 5. The N4 exhibited a small current peak at $-105°C$ corresponding to a γ-transition and a large current peak at 73°C corresponding to the glass transition. Within the temperature range of $-120-0°C$, PTMEG 2000 exhibited a current peak at $-76°C$ corresponding to the glass transition temperature of the poly-

Figure 5 TSC curves of N4E2(0.1)C, N4E2(0.3)C, and N4E3(0.2)C.

Table III   Thermal Transitions of Slowly Cooled Samples and Compression Molded Samples[a] Determined by TSC

Sample	T_γ (°C)	T_gS (°C)	T_mS (°C)	T_gH (°C)
N4	−105	—	—	71
N4C	−105	—	—	73
N4E1(0.1)	−105	3	—	65
N4E1(0.1)C	−104	−17	—	52
N4E1(0.2)	−105	−27	—	52
N4E1(0.2)C	−104	−38	—	43
N4E1(0.3)	−105	−34	—	47
N4E1(0.3)C	−104	−39	—	40
N4E2(0.1)	−108	−32	—	54
N4E2(0.1)C	−105	−54	—	45
N4E2(0.2)	−105	−53	—	34
N4E2(0.2)C	−105	−55	—	34
N4E2(0.3)	−110	−57	—	38
N4E2(0.3)C	−105	−60	13	—
N4E3(0.1)	−105	−72	16	—
N4E3(0.1)C	−105	−69	22	—
N4E3(0.2)	−110	−70	18	—
N4E3(0.2)C	−105	−69	15	—
N4E3(0.3)	−110	−70	17	—
N4E3(0.3)C	−105	−69	11	—

[a] Indicated by "C" after the original notation.

ether glycol. It can be seen that N4E2(0.1)C exhibited three current peaks at −105, −54, and 45°C, respectively. The current peak at −105°C corresponded to a γ-transition. This γ-transition has been ascribed to be caused by the local chain motion for some *block*-copolyetheresters.[13] Because PTMEG 2000 showed no such transition but N4 did, the γ-transition of N4E2(0.1)C and other *block*-copolyetherester samples corresponded to the local chain motion of the polyester segments. Comparing with the DSC data, the current peak at −54°C corresponded to T_gS and that at 45°C corresponded to T_gH. The N4E3(0.2)C exhibited three current peaks at −108, −69, and 13°C. No doubt, the current peak at −108°C corresponded to a γ-transition and that at −69°C corresponded to T_gS. Comparing with the DSC data, the current peak at 13°C seemed to be associated with T_mS rather than T_gH. The T_gH could not be detected by TSC for the N4E3(x) samples possibly because of the presence of the T_mS. The relaxation of the oriented dipoles during melting of the polyether segments might be enormous and the charging effect[21] might be significant; these effects might interfere with the T_gH peak to be detected. A similar situation also

was met for N4E2(0.3)C, which exhibited a T_mS of 15°C and whose T_gH peak seemed to be overlapped by the T_mS peak as shown in Figure 5. The transition temperatures of the slowly cooled and compression molded samples determined by TSC are tabulated in Table III.

As shown in Table III, all the samples exhibited a similar γ-transition at about −105°C independent of the composition and the thermal history (slowly cooled or compression molded). The N4 sample and N4C exhibit a similar T_gH indicating that compression molding has little influence on T_gH of N4. The T_gS values of slowly cooled N4E3(x) samples and N4E3(x)Cs were around −70°C and independent of the composition and the thermal history. Because the amorphous parts of the polyether segments in this N4E3(x) series of *block*-copolyetheresters would be immiscible with the amorphous parts of the polyester segments, compression molding did not affect the T_gS. This is consistent with the DSC data. However, compression seemed to depress the T_gS and T_gH for N4E1(x) and N4E2(x) series of *block*-copolyetheresters as shown in Table II. The decrease in T_gS after compression molding for N4E1(0.1) and N4E2(0.1) was markedly greater than others. Figure 6 compares the depolarization profiles of slowly cooled N4E1(0.1) and N4E1(0.1)C. Because the depolarization current in TSC measurement is caused by the relaxation of the oriented dipoles associated with the molecular motion, a significant increase in the depolarization current may indicate the onset of the molecular motion corresponding to a thermal transition of interest. It can be seen from Figure 6 that

Figure 6   TSC curves of slowly cooled N4E1(0.1) sample and N4E1(0.1)C.

Figure 7 Tan δ versus temperature curves and G' versus temperature curves of N4E1(x)Cs.

Figure 8 G' versus temperature curves of N4E2(x)Cs and N4E3(x)Cs.

T_gS peak of slowly cooled N4E1(0.1) sample was broader than N4E1(0.1)C, but the onset temperatures of molecular motion were similar. A greater shift in peak temperature to a lower temperature was found after compression molding for N4E1(0.1). A decrease in the content of polyester segments in the polyether soft phase may have caused this result. As also shown in Figure 6, a shift in peak temperature of T_gH to a lower temperature was observed. An increase of the content of polyether segments in the amorphous polyester hard phase may cause such a result. Because the amorphous parts of the polyether segments in N4E1(x)s and N4E2(x)s series might be partially miscible with the amorphous parts of the polyester segments, a crystalline polyester phase and two amorphous phases that contain a principle type of segment with another minor type of segment might exist. The amorphous hard phase is rich in polyester segments and the amorphous soft phase is rich in polyether segments. Because compression molding increased the crystallinity of the polyester segments, the content of amorphous polyester parts decreased accordingly. This effect decreased the content of polyester segments in the amorphous soft phase and lowered the T_gS. Similarly, the content of polyester segments in the amorphous hard phase decreased after compression molding, the effect of the polyether segment is raised and T_gH was lowered.

DMA

The dynamic mechanical properties of the compression molded *block*-copolyetherester samples

were determined. Figure 7 shows the dynamic mechanical curves of N4E1(x)Cs and Figure 8 shows the G' versus temperature curves of N4E2(x)Cs and N4E3(x)Cs. It can be seen from the tan δ versus temperature curves that all *block*-copolyetheresters exhibited a major damping peak corresponding to the glass transition of the polyether phase T_gS. The T_gS values are listed in Table IV. The trend in T_gS measured by DMA is consistent with those determined by DSC and TSC. The N4E1(x)Cs and N4E2(x)Cs exhibited a small broad damping peak at about $-96°C$. This γ-transition peak was not affected by the composition and attributed to the local chain motion of the polyester segments. This result also is consistent with that of TSC. It should be noted

Table IV Thermal Transitions of Compression Molded Samples Determined by DMA

Sample	T_γ (°C)	T_gS (°C)
N4E1(0.1)C	-96	10
N4E1(0.2)C	-103	-23
N4E1(0.3)C	-97	-33
N4E2(0.1)C	-96	-29
N4E2(0.2)C	-96	-48
N4E2(0.3)C	-91	-48
N4E3(0.1)C	—	-63
N4E3(0.2)C	—	-63
N4E3(0.3)C	—	-63

that the transition temperatures measured by DMA were higher than those determined by DSC and TSC because of the dynamic nature for DMA. But no γ-transition could be detected by DMA for N4E3(x)Cs possibly because of the low weight content of polyester segments in this series of *block*-copolyetheresters.

It can be seen from Figures 7 and 8 that composition had significant influence on the G' versus temperature relationships of the *block*-copolyetheresters. Below T_gS, the real part of the dynamic modulus, log G' decreased slowly as the temperature was raised for N4E1(x)Cs and N4E2(x)Cs. Then log G' decreased drastically with the increase of temperature around T_gS. Above T_gS, log G' decreased gradually with the increase of temperature. The N4E3(x) seemed to exhibit some different G' versus temperature relationships. In addition to a drastic drop in log G' around T_gS, in the temperature range of $-10-15°C$, log G' decreased drastically with temperature. This might be associated with the melting of the polyether segments. The G'-value of the *block*-copolyetheresters above 25°C decreased as the content of the polyether segments increased, as expected, as shown in Figures 7 and 8. The abrupt drop in log G' in the temperature range of $-10-15°C$ for N4E3(x)Cs caused by the melting of the polyether segments indicates that the crystalline properties of the polyether segments will affect the mechanical properties of the *block*-copolyetheresters.

CONCLUSIONS

Compression molding had significant influence on the thermal transitions and crystalline properties of *block*-copolyetheresters. The crystallinity of the polyester segments was enhanced significantly after compression as indicated by the DSC and X-ray diffraction results. After compression molding, the diffraction peaks were changed completely indicating that the crystalline structure of the polyester segments was changed to a denser crystalline structure. The T_gS and T_gH of N4E1(x)s and N4E2(x)s were depressed after compression molding as indicated by the DSC and TSC results. This is described as the compression molding increasing the crystallinity of the polyester segments and thus decreasing the content of polyester segments in the amorphous polyether soft phase as well as in the amorphous polyester phase. This decreased T_gS and T_gH. The DMA results indicate the presence of a γ-transition, T_gS, and the effect of composition on the modulus-temperature relationships. The abrupt drop in log G' in the temperature range of $-10-15°C$ for N4E3(x)Cs caused by the melting of the polyether segments suggests that the crystalline properties of the polyether segments could affect the mechanical properties of the *block*-copolyetheresters.

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